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A MODIFIED LEPS SURFACE FOR CARBON DIOXIDE

Arthur Gauss, Jr.

November 1978

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
BALLISTIC RESEARCH LABORATORY
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A modified LEPS potential surface has been developed for the ground state of the carbon dioxide molecule. Both the Sato parameter and the Morse equilibrium distances (r_{io}'s) have been made functions of the coordinates. A very flexible LEPS surface is thus created which fits many of the known properties of the CO_2 potential.

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I. INTRODUCTION

The analytical potential surface described here for carbon dioxide has found application in infrared radiation suppression from aircraft exhaust plumes[1]. This work could be useful to the target signature work planned for BRL in the near future.

Analytical potential surfaces are very useful for dynamics calculations from which cross sections and rate constants of chemical reactions are determined. The analytical surface is fitted to the known properties of the potential surface derived from experiment and ab initio calculations. The fitting surface can then provide the derivatives with respect to the internuclear coordinates over all space necessary for the dynamics calculation.

The CO_2 surface developed here is a specially modified LEPS potential. It agrees well with known properties of the CO_2 ground state surface[2]. Considerable success has been achieved at the BRL in modifying LEPS surfaces to give good approximations to molecular potentials for other systems as well, i.e., H_2O, HO_2[3,4]. Full dynamics calculations have been carried out on the HO_2 surface[4]. This report gives a complete description of the CO_2 potential surface only; no dynamics have yet been attempted.

II. MODIFIED LEPS POTENTIAL FOR CO_2

CO_2 is a linear molecule with atoms arranged in O-C-O order. The minimum of potential energy in this linear configuration (θ=180°) is 7.5 eV below the separated $CO(^1\Sigma^+)$ + $O(^1D)$ state[2]. The C-O equilibrium bond distances[2] are equal to 1.16 Å.

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1. Air Force Office of Scientific Research Contract F49620-77-C-0056, "Analysis of a Model for IR Suppression", George Wolken, Jr. Battelle Columbus Laboratories.
2. Herzberg, G., Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand Reinhold Company, NEw York, pp 429-437, (1966).
3. Gauss, A., "A Modified LEPS Surface for the Ground State of the Water Molecule", Chemical Physics Letters, Vol. 52, No. 2, pp. 252-254 (1 Dec. 1977).
4. Gauss, A., "Trajectory Calculations on the $H+O_2 \rightarrow OH+O$ Combustion Reaction", J. Chem. Phys., Vol. 68, No. 4, pp. 1689-1694 (15 Feb 1978).

The modified LEPS surface has a minimum well depth (at $\theta = 180°$) of 7.8 eV below the CO ($^1\Sigma^+$) + O(^{1}D) state with C-O equilibrium bond distances equal to 1.13Å. These values are in good agreement with Herzberg[2].

The general form of the LEPS surface is given by[5]

$$V = Q_1' + Q_2' + Q_3' - (\alpha_1'^2 + \alpha_2'^2 + \alpha_3'^2 - \alpha_1'\alpha_2' - \alpha_2'\alpha_3' - \alpha_3'\alpha_1')^{1/2} + D_2^e$$

where

$$Q_i' = \frac{Q_i}{(1+\Delta_i)} = \frac{D^e_i}{4(1+\Delta_i)} \quad (3+\Delta_i)e^{-2\beta_i(r_i-r_{io})} - (2+6\Delta_i)e^{-\beta_i(r_i-r_{io})}$$

and

$$\alpha_i = \frac{\alpha_i}{(1+\Delta_i)} = \frac{D^e_i}{4(1+\Delta_i)} \quad (1+3\Delta_i)e^{-2\beta_i(r_i-r_{io})} - (6+2\Delta_i)e^{-\beta_i(r_i-r_{io})}$$

D_i^e and β_i are the standard Morse parameters and are shown in Table I.[6,7] The r_{io}'s have been made functions of the internuclear coordinates as have the Sato parameters (Δ_i's). See Figure 1 for definition of the coordinates.

TABLE I. Morse Parameters for the O_2 and C-O Diatomics.

C-O	O-O
$D_1^e = D_2^e = 259.28 \frac{kcal}{mole}$	$D_3^e = 120.21 \frac{kcal}{mole}$
$\beta_1 = \beta_2 = 2.30$ Å^{-1}	$\beta_3 = 2.65$ Å^{-1}

5. Muckerman, J.T., "Classical Dynamics of the Reaction of Fluorine Atoms with Hydrogen Molecules. II. Dependence on the Potential Energy Surface", J. Chem. Phys., Vol 56, No. 6, pp. 2997-3006, 15 March 1972.
6. Herzberg, G., Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules, D. Van Nostrand Company, Inc., New York, pp. 520-521, (1950).
7. Krupsenie, P., "The Spectrum of Molecular Oxygen", J. of Phys. Chem. Ref. Data, Vol 1, No. 2, pp. 456-457 (1972).

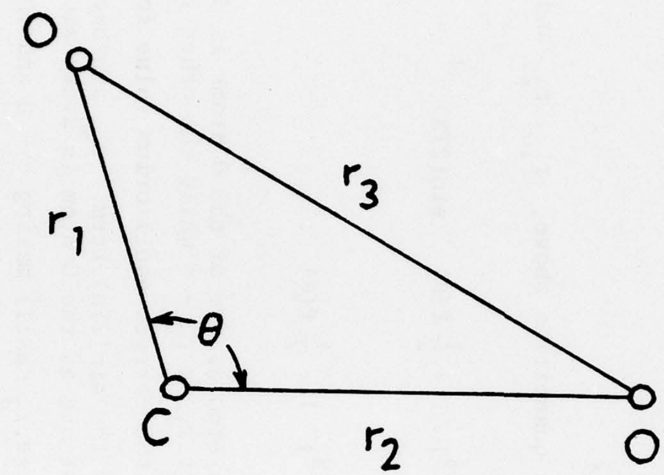

Figure 1. The internuclear distances (r_1, r_2, r_3) and the angle θ are defined as shown.

Certain quantities must now be defined

$$A_1 = {}^{27}/_{4\pi^3}$$

$$A_2 = {}^{27}/_{2\pi^2}$$

$$A_3 = {}^{27}/_{4\pi} \quad .$$

$$f(\theta) = A_1\theta^3 + A_2\theta^2 + A_3\theta$$

and

$$Th = \text{Arc tan} \; {}^{r_1}/_{r_2} \quad .$$

Having defined the quantities above, r_{10}, r_{20} and r_{30} (all in cm.) can now be given:

$$r_{10} = (1.128 \times 10^{-8}) \quad 1 + \frac{1}{2} f(\theta) \quad \sin(2Th) \quad ^4$$

$$r_{20} = r_{10}$$

$$r_{30} = (1.207 \times 10^{-8}) \quad 1 + \frac{1}{2} f(\theta) \quad .$$

In the triatomic system as one of the O atoms is drawn away leaving a CO molecule (if either r_1 or $r_2 \to \infty$ while the other is finite) then r_{10} and $r_{20} \to 1.128$ Å, the correct equilibrium value for CO.[6] This behavior is dictated by the sin(2Th) term. r_{30} approaches the correct O_2 equilibrium bond distance as the C atom is drawn away from the O_2 molecule (r_1 and r_2 large, r_3 small) making $\theta \to 0$ and thus $f(\theta) \to 0$.

The Sato parameters are all taken to be equal and are defined by

$$\Delta_i = \Delta = 7.7 \; (\sin \frac{\theta}{2}) \quad \frac{r_1 \cdot r_2}{r_{10}^{\;2}} \quad \cdot \exp \quad - \frac{2r_1r_2}{r_{10}^{\;2}}$$

$i = 1,2,3.$

The Sato parameter varies from a maximum of 1.05 near the CO_2 equilibrium position to a minimum of 0 as r_1 or r_2 or both become large.

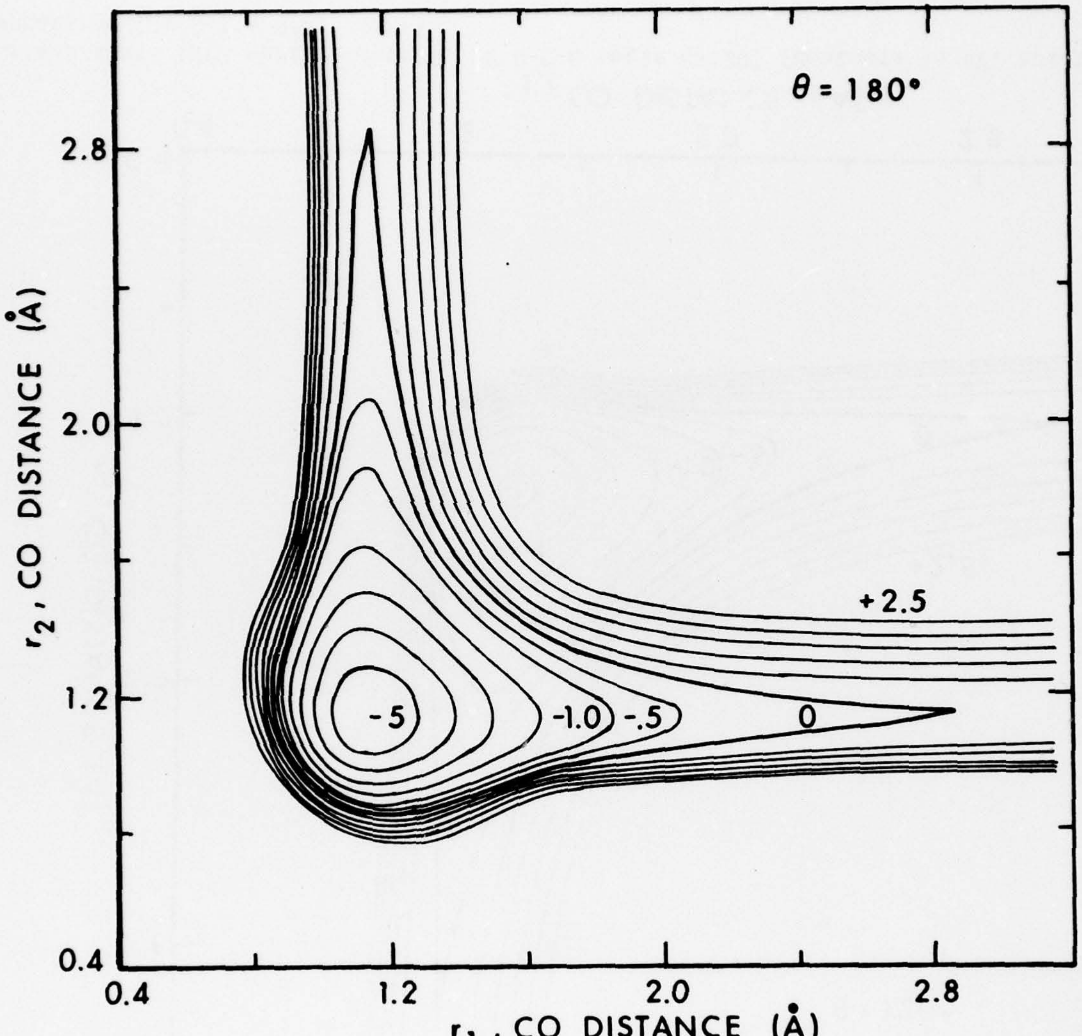

Figure 2. Ground state LEPS surface for CO_2 for O-C-O angle θ=180° (contours in eV. relative to the separated $CO(^1\Sigma^+)$ + $O(^3P)$ state).

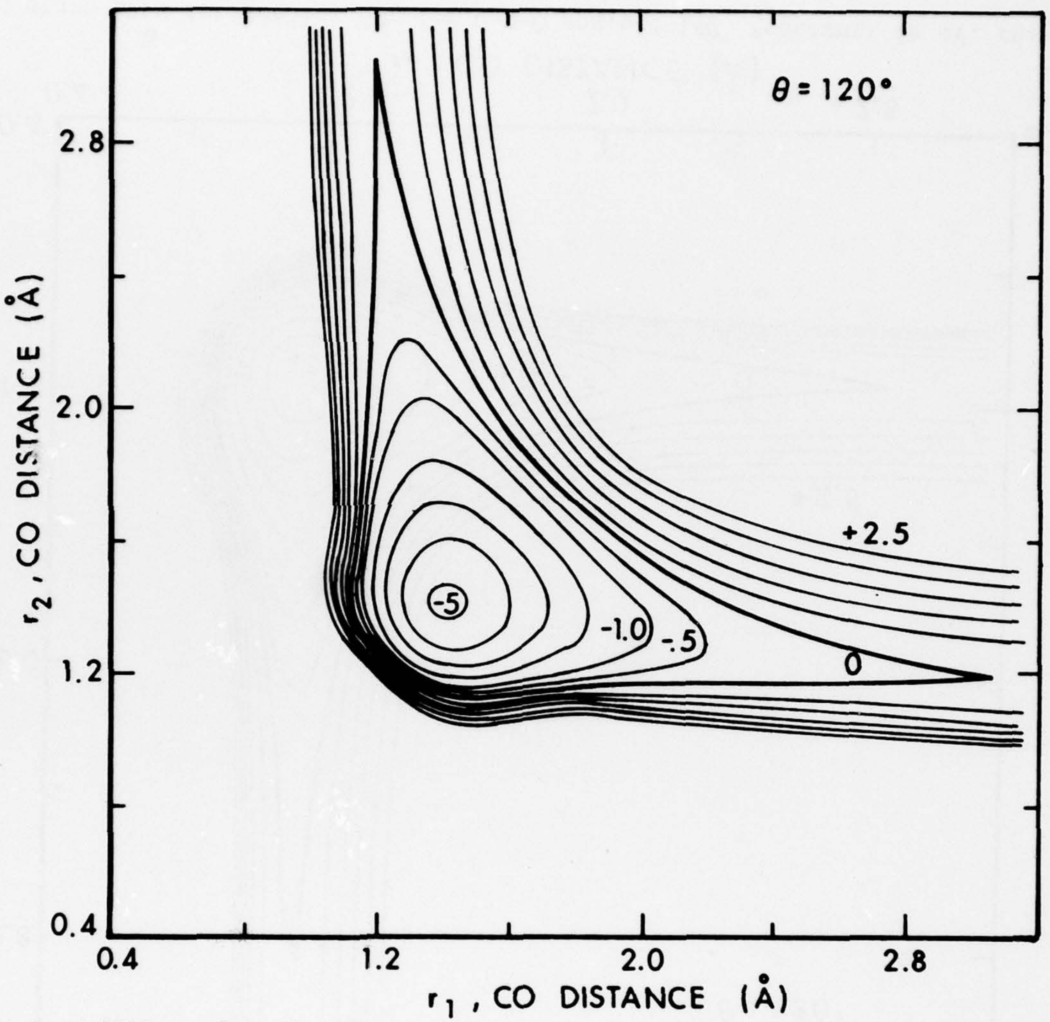

Figure 3. Ground state LEPS surface for CO_2 at O-C-O angle θ=120° (contours in eV. relative to the separated $CO(^1\Sigma^+)$ + O^3P) state).

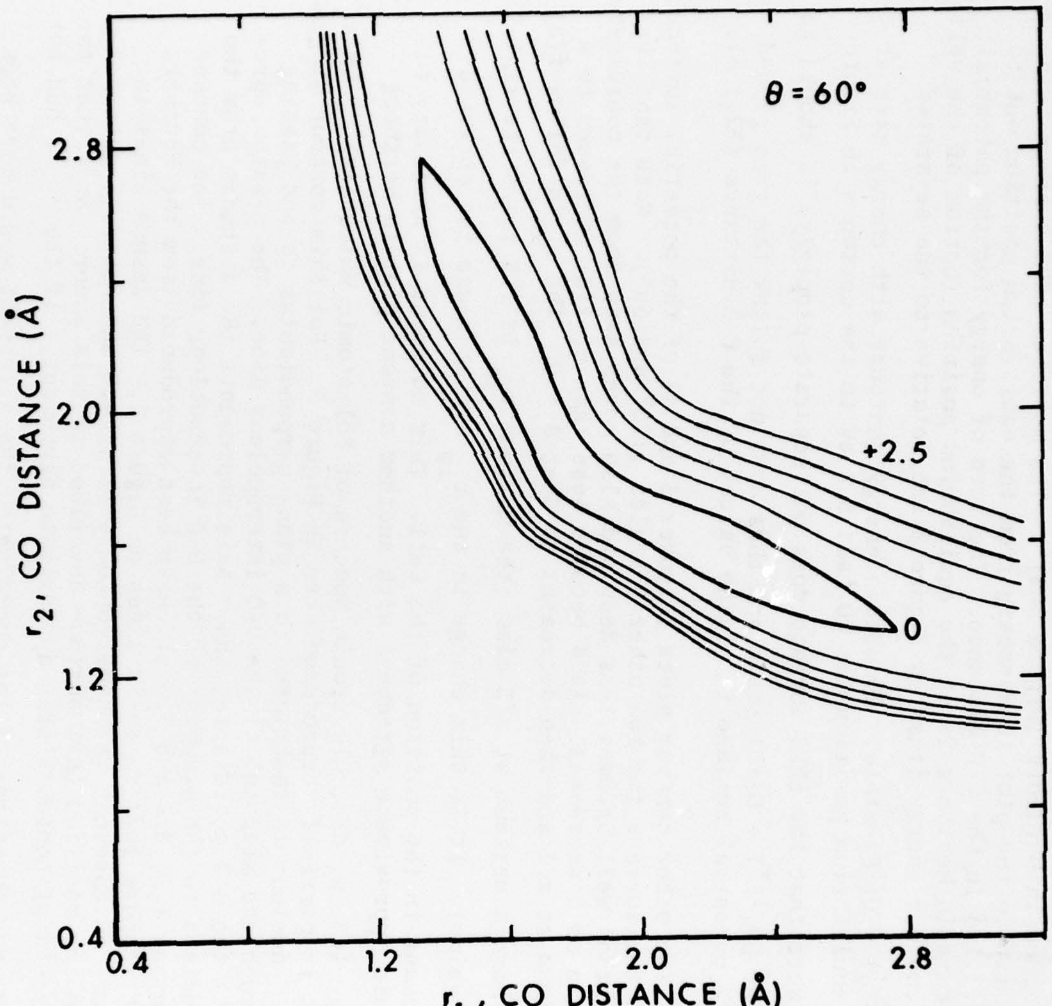

Figure 4. Ground state LEPS surface for CO_2, O-C-O angle θ=60° contours in eV. relative to the separated $CO(^1\Sigma^+) + O(^3P)$ state)[2].

Contour surface plots of the LEPS surface (V) are shown in Figures 2, 3 and 4. Figure 2 shows the linear configuration $\theta = 180°$. This plot compares favorably with the linear configuration contour plot contained in Herzberg (Figure 163)[2]. The modified LEPS surface is a good fit to the plot in Herzberg from the equilibrium position out to some 2.1 Å in the C-O distance. The zero of energy for the potential contours in Herzberg is at the equilibrium position (bottom of the well). The contour energy lines in Figure 2 are relative to the separated $CO(^1\Sigma^+) + O(^3P)$ state. To obtain energy contours with energy zero at the equilibrium position for CO_2 add 5.8 eV to the contours in Figure 2. Note that the LEPS surface does not separate properly, it should go to the $CO(^1\Sigma^+) + O(^1D)$ state and thus does not follow the true ground state potential surface for large values of the C-O distance (>2.1 Å).

The other contour plots (Figures 3 and 4) of the potential surface show the surface for two other θ angles (120° and 60°). Note that the potential well becomes less deep and also moves away from the coordinate origin as θ decreases. As θ becomes less than π, $f(\theta)$ increases to a maximum at $\pi/3$ and then decreases to 0 at $\theta = 0$. The r_{io}'s follow $f(\theta)$ and have a maximum at $\pi/3$ also (the maximum r_{io} is 1.5 times the minimum value). It is this change in the r_{io}'s that cause the observed movement in the position of the well. This movement is necessary to obtain approximate agreement with another contour plot in Herzberg (Fig. 167, p. 436, Electronic Spectra of Polyatomic Molecules)[2]. This plot is partially reproduced here in Figure 5. For this contour diagram the C nucleus is restricted to a plane perpendicular to and passing through the midpoint of the O-O internuclear line. The x-axis represents the O-O coordinate; the y axis represents the distance from the C nucleus to the midpoint of the O-O internuclear line. The contour lines at 1.5, 4.5 and 7.5 eV. have been reproduced from the Herzberg plot (Figure 167) as solid lines on Figure 5. The dashed lines in Figure 5 represent the same contours (1.5, 4.5 and 7.5 eV.) obtained from the modified LEPS surface described in this paper. Note that the two sets of contours show approximate agreement. If the r_{io}'s had not been made functions of the coordinates the agreement would have been much worse. The LEPS points along x-axis would remain the same but the LEPS contours would incline sharply to the left for small values of the y-coordinate. Most of the inclosed area of these LEPS contours would be to the left of the Herzberg contours and the LEPS contours shown in Figure 5.

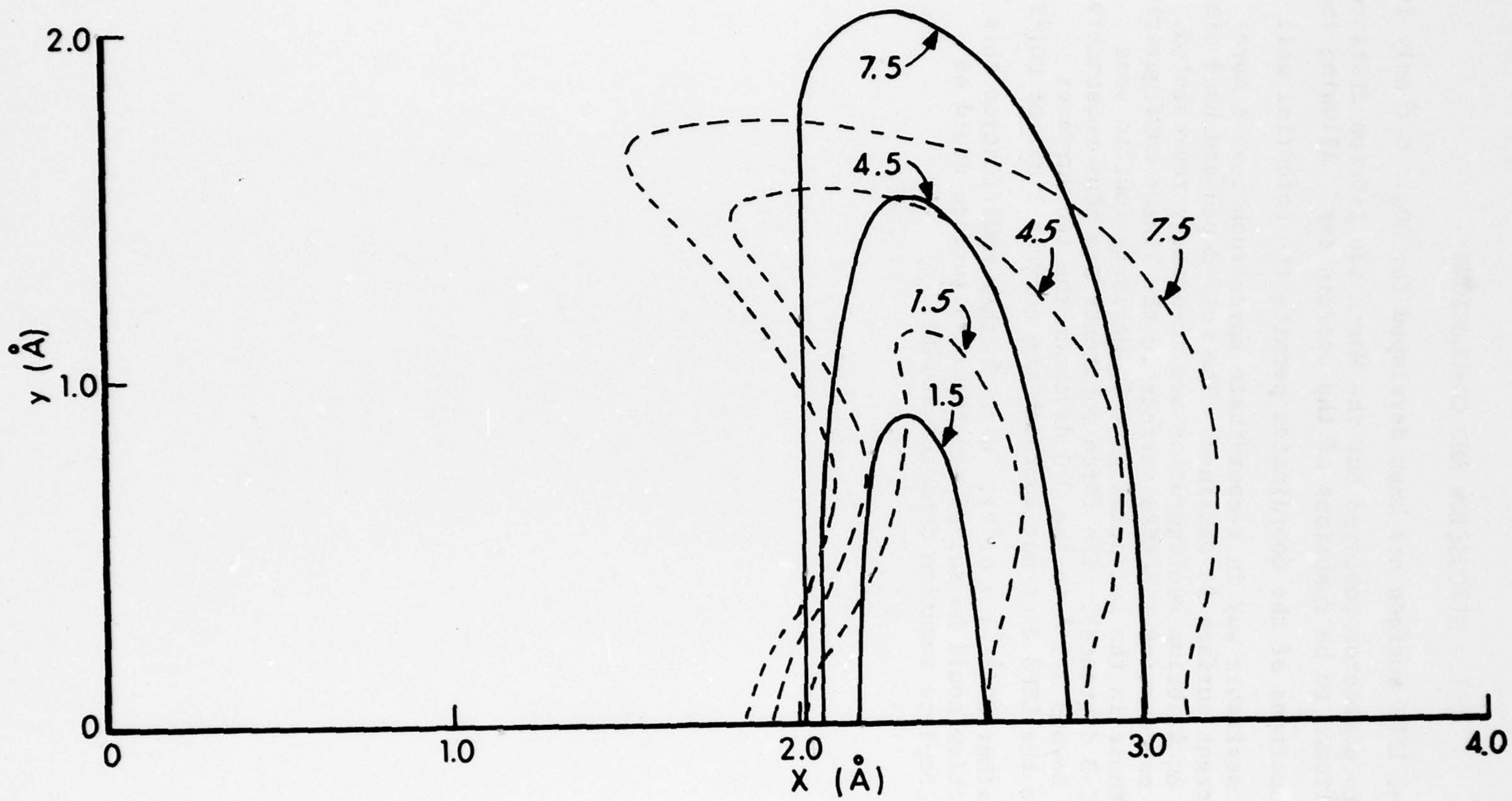

Figure 5. Comparison of the contours of the Herzberg surface[2] (solid lines) and the modified LEPS surface (dashed lines) for the ground state of CO_2. The contours are plotted as a function of the 0-0 distance (x) and the perpendicular distance (y) of the C nucleus from the 0-0 line.

III. DISCUSSION AND CONCLUSIONS

A modified LEPS surface has been developed for CO_2. Not only is a variable Sato parameter employed but the Morse equilibrium distances (r_{io}'s) are allowed to be functions of the coordinates. Allowing the r_{io}'s to be functions of the coordinates permits the potential well to be moved in a desirable way in r-coordinate space such that a more completely correct surface is obtained. The well depth and bond distances in the equilibrium configuration are adequately represented. The potential contours of the LEPS surface in the linear configuration are close to those in the potential plot in Herzberg (out to some 2.1 Å in the C-O distance). The force constants are thus reasonably represented. Beyond 2.1 Å in the C-O distance the two surfaces separate since the LEPS does not approach the correct limit of $CO(^1\Sigma^+) + O(^1D)$ but rather $CO(^1\Sigma^+) + O(^3P)$. With further modification this separation problem could be solved and the LEPS surface would be suitable for complete reaction dynamics studies.

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